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EFFECTS OF HEATING ON TEFLON® FEP THERMAL CONTROL MATERIAL FROM THE HUBBLE SPACE TELESCOPE

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ABSTRACT

Metallized Teflon® FEP (fluorinated ethylene propylene) thermal control material on the Hubble Space Telescope (HST) is degrading in the space environment. Teflon® FEP thermal control blankets (space-facing FEP) retrieved during the first servicing mission (SM1) were found to be embrittled on solar facing surfaces and contained microscopic cracks. During the second servicing mission (SM2) astronauts noticed that the FEP outer layer of the multi-layer insulation (MLI) covering the telescope was cracked in many locations around the telescope. Large cracks were observed on the light shield, forward shell and equipment bays. A tightly curled piece of cracked FEP from the light shield was retrieved during SM2 and was severely embrittled, as witnessed by ground testing. A Failure Review Board (FRB) was organized to determine the mechanism causing the MLI degradation. Density, x-ray crystallinity and solid state nuclear magnetic resonance (NMR) analyses of FEP retrieved during SM1 were inconsistent with results of FEP retrieved during SM2. Because the retrieved SM2 material curled while in space, it experienced a higher temperature extreme during thermal cycling, estimated at 200 °C, than the SM1 material, estimated at 50 °C. An investigation on the effects of heating pristine and FEP exposed on HST was therefore conducted. Samples of pristine, SM1, and SM2 FEP were heated to 200°C and evaluated for changes in density and morphology. Elevated temperature exposure was found to have a major impact on the density of the retrieved materials. Characterization of polymer morphology of as-received and heated FEP samples by NMR provided results that were consistent with the density results. These findings have provided insight to the damage mechanisms of FEP in the space environment.

1. INTRODUCTION

The Hubble Space Telescope (HST) was launched on April 25, 1990 into low Earth orbit and is the first mission of NASA's Great Observatories program. It is a telescope capable of performing observations in the near-ultraviolet, visible and near-infrared (0.115 to 2.5 μm). The HST was designed to be serviced on-orbit to upgrade scientific capabilities. The first servicing mission (SM1) occurred in December 1993, after 3.6 years in space. The second servicing mission (SM2) was in February 1997, after 6.8 years in space. Servicing missions are planned for late 1999, mid 2000, and early 2003.[1]

The HST is covered with two types of thermal control materials, radiators and multi-layer insulation (MLI) blankets, which passively control temperatures on-orbit. Both of these thermal control materials utilize metallized-Teflon® fluorinated ethylene propylene (FEP) as the exterior (space-facing) layer. Teflon® FEP is used as the outer layer of thermal control insulation because of its excellent optical properties (low solar absorptance and high thermal emittance). A metallized layer is applied to the backside of the FEP to reflect incident solar energy. During SM1 astronauts retrieved and returned to Earth aluminized-FEP (Al-FEP) and silvered-FEP (Ag-FEP) MLI blanket material. The Al-FEP MLI (2 blankets retrieved) covered the two magnetometers that were replaced during SM1. The Ag-FEP MLI covered the solar array drive arm (SADA) of the retrieved solar array (the solar arrays were also replaced during SM1, and one of the two arrays could not be retracted and was jettisoned into space). Analyses of the retrieved blanket materials revealed that the 5 mil (127 μm) thick FEP exterior layer was embrittled on high solar exposure surfaces.[2,3] Surfaces which received the highest solar exposures (16,670 equivalent sun hours (ESH) for the Al-FEP, and 20,056 ESH for the Ag-FEP) had microscopic through-thickness cracks in the 5 mil FEP at stress locations.[2,3] Bonded solar facing 2 mil (51 μm) Al-FEP on the SADA power harness, which was also retrieved during SM1, had many cracks and had lost total mechanical integrity in heavily stressed areas.[4] It should be noted that the maximum temperature during thermal cycling of the power harness FEP was higher (>130°C)[4] than the magnetometer FEP (50°C)[5] due to internal heat sources.

During SM2, severe cracking of the MLI outer layer material (Al-FEP, 5 mil thick) was observed on the light shield, forward shell and equipment bays of the telescope. Astronaut observations combined with photographic documentation of HST taken during SM2, revealed extensive cracking of the MLI in many locations around the telescope (solar and anti-solar facing surfaces), with solar facing surfaces being particularly heavily damaged.[1] The FEP outer layer at several of the longest cracks was observed to be curled up and lifted away from the next MLI layer. The worst of the MLI outer layer cracks were patched during the last extravehicular activity (EVA) day. Figure 1, taken during an EVA, shows two cracked areas on the light shield. A very large vertical crack can be seen near the bottom of the photograph facing the astronauts, and a smaller cracked area which has curled-up tightly (with the FEP surface in compression) can be seen above the vertical crack. Prior to patching the upper light shield crack, the tightly curled Al-FEP outer layer was removed (cut off with scissors) and retrieved for post-mission analysis. A close-up of the tightly curled MLI section is shown just after being removed in Figure 2. After SM2, Goddard Space Flight Center (GSFC) established a HST MLI Failure Review Board (FRB). The objectives of the FRB were to determine the mechanism causing the MLI degradation, to predict the condition of MLI surfaces at the time of the third servicing

mission (SM3), to recommend the extent of MLI repair/replacement during SM3, and to recommend material to be used during SM3 for MLI repair/replacement. Extensive investigation of the optical, chemical, physical and mechanical properties of the retrieved SM2 FEP have been conducted and compared with SM1 and pristine FEP samples.[1,5,6] Simulated LEO environmental exposure testing of pristine FEP was also conducted to help determine the cause of degradation of FEP on HST.[7,8,9,10] Solar radiation (ultraviolet radiation and x-rays from solar flares), electron and proton radiation from the Van Allen belts, thermal exposure and thermal cycling, and atomic oxygen exposure are all possible LEO environmental factors which could contribute to the degradation of FEP on HST.

Figure 1. Two cracks in the MLI outer layer on the HST Light Shield photographed during a SM2 EVA. A large vertical crack is seen in the bottom of image, and a smaller cracked and tightly curled area is seen above the vertical crack.

Figure 2. Close-up of the location of the tightly curled Al-FEP MLI section that was cut off and retrieved during SM2 for post-flight analyses.

Density measurements (and calculated crystallinity) of the retrieved materials obtained under the FRB investigations indicated that FEP from SM1 was essentially unchanged from pristine FEP and that SM2 FEP had an increased density compared to pristine FEP.[5] These results were consistent with crystallinity measurements taken using x-ray diffraction (XRD) and with solid-state nuclear magnetic resonance (NMR) results.[5] Because the SM2 FEP was embrittled and its density and crystallinity were found to have increased compared to pristine FEP, it would have been expected that the SM1 FEP, which was also embrittled, would have had an increased crystallinity and density also, which it did not. Because the retrieved SM2 FEP was curled in space exposing the backside (aluminized side), this sample experienced a higher temperature extreme during thermal cycling than the SM1 material experienced. It was estimated that the curled FEP cycled between -100°C to +200°C, while the SM1 material cycled between -100°C to +50°C.[5] It was postulated that the SM2 FEP may have become more crystalline, and hence more dense in space due to the higher temperature exposure. Because the SM1 FEP should have been damaged in the same manner as SM2, but to a lesser extent (due to the lower fluences), it was proposed to heat the SM1 material to 200°C, like the SM2 material experienced in space, and measure the density after heating. Therefore, a series of tests have been performed to determine if exposure of the SM2 FEP to a higher maximum temperature on-orbit after curling (200°C compared to 50°C for nominal conditions) had an impact on the degradation mechanism of the FEP. Two different characterization techniques (density and solid-state NMR characterization) were used to evaluate the effect of elevated temperature exposure on SM1 FEP, SM2 FEP and pristine Al-FEP samples. The density of Al-FEP samples that were thermal cycled to HST nominal temperature extremes, and samples exposed to simulated solar flare x-rays (with and without elevated temperature exposure) were also obtained to help understand the damage mechanism of FEP on HST.

2. MATERIALS AND EXPERIMENTAL PROCEDURES

2.1 Materials

Materials evaluated for physical density and solid-state NMR were pristine Al-FEP, SM1 FEP (Al-FEP) and SM2 FEP (Al-FEP). SM1 Ag-FEP from the SADA was not characterized because it was adhesively bonded to a scrim substrate.

2.1.1 Pristine Al-FEP The pristine material was 5 mil (127 μm) FEP coated on the backside with 1000 Å of vapor deposited Al (VDA).

2.1.2 HST SM1 FEP The SM1 FEP material was from the outer layer of one of the two-retrieved magnetometer (or magnetic sensing system (MSS)) electronics box MLI blanket covers. The retrieved MSS MLI blankets are shown in Figure 3. These thermal blankets are roughly 35 cm x 38 cm in size. The outer layer was composed of 127 μm FEP coated on the backside with 1000 Å of VDA. The MLI blankets were wrapped around the electronics boxes such that each blanket had 5 different areas that experienced difference solar exposures on-orbit.[2]

Figure 3. Photograph of the two MSS MLI blankets retrieved during SM1.

2.1.3 HST SM2 FEP The SM2 FEP material was from the cracked and tightly curled outer layer of the MLI blanket covering the upper light shield (see Figure 2). The outer layer was composed of 127 μm FEP coated on the backside with 1000 Å of VDA, and this sample had curled with the FEP surface in compression to a diameter of 1.5 cm.[5] Two areas of the retrieved SM2 FEP sample were analyzed. One piece was from inside the tightly curled area, which experienced the +200°C temperature extreme when curled. The second piece was from the "flat" section of the retrieved sample, next to the astronaut cut area where the FEP had started to curl. This flat area most likely did not get as hot as the tightly curled area.

2.1.4 Simulated Solar Flare X-Ray Exposed and Thermal Cycled FEP The materials that were exposed to simulated solar flare x-rays were Al-FEP (127 μm FEP coated with 1000 Å VDA), and Ag-FEP (127 μm FEP/650 Å Ag/90 Å Inconel). The material that was thermal cycled was Al-FEP (127 μm FEP coated with 1000 Å VDA).

2.2 Environmental Exposure

2.2.1 HST Environment Exposure The HST sample designations and their corresponding LEO environmental exposures are listed in Table 1.[10] The two magnetometers are placed on HST such that the MLI blankets covering their electronics boxes received identical but symmetrical exposures. Unfortunately, the MSS blankets were not labeled when retrieved during SM1, therefore the solar exposures of two of the sides could not be positively identified. The SM2 sample was retrieved from the solar facing side (+V3) of the telescope.

Table 1. Environmental Exposures for Retrieved HST Thermal Control Materials.

HST Sample	Equivalent Sun Hours (ESH)	Thermal Cycling	X-ray Fluence (J/m^2)	Trapped e^-/p^+ >40 keV ($\#/cm^2$)	Atomic Oxygen ($\#/cm^2$)
SM1 MSS-A	16,670 (16% albedo)	19,700 cycles -100/+50 °C	0.5-4Å: 12 1-8Å: 175	e^-: $1.4x10^{13}$	$<1.5x10^{20}$
SM1 MSS-B/C	6,324 or 9,193 (72 or 33% alb.)		0.5-4Å: 2 or 5 1-8Å: 22 or 77	p^+: $8.0x10^9$	$<<1.5x10^{20}$
SM1 MSS-D	11,339 (7% albedo)		0.5-4Å: 9 1-8Å: 132		$<3.1x10^{20}$
SM1 MSS-E/F	9,193 or 6,324 (33 or 72% alb.)		0.5-4Å: 5 or 2 1-8Å: 77 or 22		$<<1.5x10^{20}$
SM1 MSS-G	4,477 (100% albedo)		0		$<1.5x10^{20}$
SM2 Curled	33,638 direct (0% albedo)	37,100 cycles *-100/+200 °C when curled*	0.5-4Å: 16 1-8Å: 252	e^-: $2.0x10^{13}$ p^+: $2.0x10^{10}$	$<3.2x10^{20}$
SM2 Flat		*100/<+200 °C when curled*			

2.2.2 Simulated Solar Flare X-Ray Exposure Pristine Al-FEP and Ag-FEP samples were exposed to simulated solar flare x-rays in a modified electron beam evaporator system operated at 10^{-6} to 10^{-7} torr. Samples were irradiated with x-rays in the energy range that can be absorbed in the bulk of the 127 μm thick FEP to simulate the embrittlement witnessed in LEO. Simulated solar flare x-ray testing is described in detail in references 8 and 11. Sample FEP4D (Ag-FEP) was irradiated with 9 keV non-monochromatic (continuous and characteristic line radiation) aluminum x-rays for 5 hours. Sample FEP7D and FEP7B (both Al-FEP) were irradiated with 8 keV non-monochromatic molybdenum x-rays for 5 hours. These exposures resulted in similar embrittlement of the 5 mil FEP based on tensile testing, as the SM1 FEP.

2.2.3 Static Heat Treatment Samples for physical density characterization were exposed to 200 °C at ambient pressure in a furnace oven. Pristine Al-FEP samples were heat treated for 1 to 21 days. HST SM1 and SM2 samples were heat treated for 5 to 21 days. The x-ray exposed samples were heat treated for 13 days. Samples of pristine FEP and SM1 FEP (MSS-D, 11,339 ESH) were also exposed in furnace ovens to temperatures of 50 °C, 75 °C, 100 °C, 125 °C, 150 °C, 175 °C and 200 °C for a period of 3 weeks. NMR samples were heated in an oven at a temperature of 190 °C for 6 days.

2.2.4 Thermal Cycling A sample of pristine 127 μm Al-FEP was thermal cycled between −100 °C and +50 °C (the nominal temperature range for solar facing MLI surfaces) for 6,000 cycles at a rate of approximately 7 minutes per cycle. Thermal cycling test procedures for the −100 °C to +50 °C testing are detailed in reference 11. A second pristine Al-FEP sample was thermal cycled for 20,000 thermal cycles from −196 °C to +74 °C to simulate the anti-solar facing side of HST, which cycles from −200 °C to −10 °C on-orbit.[10] A soft x-ray exposed

sample was thermal cycled from −196 °C to +74 °C for 2,688 cycles. The facility used for the −196 °C to +74 °C thermal cycling is described in detail in reference 10. Samples were thermal cycled between −196 °C and +74 °C at a rate of 12 seconds per cycle, except for every seventh cycle (16 seconds per cycle) where samples reached an upper temperature limit of 130 °C. The upper limit was chosen so that the samples did not build up an accumulation of frost.

2.3 Characterization

2.3.1 Density Density measurements were obtained using calibrated density gradient columns. The density solvents used were carbon tetrachloride (CCl_4) which has a density of 1.594 g/cm^3, and bromoform ($CHBr_3$) which has a density of 2.899 g/cm^3. Solutions of two different densities are added to a 50 mL buret, along with five standards of known densities (± 0.0001 g/cm^3). Data was obtained by placing very small pieces of unheated or heated samples into the column and noting their linear position. The sample densities were then obtained from the curve fitted for the standards. Data was obtained from four separate density columns. The presence of, or absence of the VDA coating (as removed by NaOH solution) was found to have no effect on the density of the Al-FEP samples, therefore the Al was left on the majority of samples during density characterization.

2.3.2 Solid State Nuclear Magnetic Resonance (NMR) Solid-state NMR was used to investigate both the presence of new chemical species (-CFX-) within the exposed FEP films as well as morphological changes that may have occurred after prolonged space exposure or due to heating. These changes were probed by monitoring the natural abundance ^{13}C spectra (radio frequency absorption), T_{CF} curves and T1ρ(C) data. $1/T_{CF}$ is a rate constant defining the growth of the ^{13}C signal intensity during cross-polarization between the fluorines and carbons. 1/T1ρ(C) is a rate constant defining the reduction of the ^{13}C signal after the application of a RF pulse to observe the ^{13}C signal. Because of the conductivity of the Al layer, the Al needed was removed prior to NMR analysis. After verifying that removal caused no change in the NMR results of a pristine sample, the Al layer was removed from all samples by washing the materials in a NaOH solution. Three samples, as-received and after heating, were analyzed for chemical and morphological changes by NMR: pristine FEP, SM1 FEP (MSS-D) exposed to 11,339 equivalent sun hours (ESH), and SM2 FEP from the tightly curled area. The pristine FEP was 1 x 18 cm, the SM1 sample was 1 x 4 cm, and the SM2 sample was only 5 mm x 5 cm. Each sample was rolled up and slid into a NMR rotor with an inner diameter of 5 mm. The specific details of NMR testing can be found in reference 12.

3. RESULTS AND DISCUSSION

3.1 Physical Density Results

Table 2 lists the density measurements of as-received and heated, pristine and HST Al-FEP. The as-retrieved densities of all five surfaces of the analyzed MSS blanket (4,477 ESH to 16,670 ESH) are the same (2.141 ± 0.001 g/cm^2) as pristine Al. The density of the SM2 material (in the tightly curled area) was significantly higher (2.183 g/cm^2). These results are consistent with the FRB findings reported in reference 5. As previously mentioned, because the SM2 material is more dense than pristine FEP, it would be expected that the SM1 material would be more dense

than pristine FEP based on the fact that the SM1 FEP is also embrittled. In tensile tests, the SM1 FEP (from the 11,339 ESH surface) had a 21% elongation to failure relative to pristine FEP (which has an elongation to failure of ≈200%),[8] and the SM2 FEP (curled area) had ≈0% plastic elongation to failure.[5]

Table 2. Density of As-Received and Heated Pristine and HST FEP Samples.

Sample	Solar Fluence (ESH)	Temperature during Space Exposure	Density As-Received (g/cm^3)	Density after 200°C (g/cm^3)	Heating Density Change	Heating Time (Days)
Al-FEP	-	-	2.141	-	-	-
Al-FEP	-	-	2.138	2.160	0.022	7
SM1 MSS-G	4,477	-100 to +50 °C	2.141	2.163	0.022	9
SM1 MSS-F	6,324 or 9,193	-100 to +50 °C	2.139	2.166	0.027	9
SM1 MSS-C	9,193 or 6,324	-100 to +50 °C	2.141	2.166	0.025	5
SM1 MSS-D	11,339	-100 to +50 °C	2.141	2.173	0.032	9
SM1 MSS-A	16,670	-100 to +50 °C	2.143	2.174	0.031	9
SM2 Curled	33,638	*-100/+200 °C when curled*	2.183	2.184	0.001	5
SM2 Flat	33,638	*-100/<+200 °C when curled*	2.155	2.177	0.022	7
FEP4D Al x-ray	-	≈ 20 °C	2.143	2.175	0.032	13
FEP7D Mo x-ray	-	≈ 20 °C	2.147	2.179	0.032	13

Heating the SM1 material at 200 °C for 5-9 days resulted in an increase in density for all samples, with increasing density with higher solar exposure (a density increase of 0.022 for 4,477 ESH, to a density increase of 0.031 for 16,670 ESH). This is still lower than the density of the as-received SM2 FEP that was heated on-orbit to 200 °C and had a higher solar exposure. The SM2 curled sample was also heated in ground-tests and did not increase in density, as had been postulated. These results prompted an interest to measure the density of a piece of SM2 FEP located adjacent to the astronaut cut. It was expected that this "flat" SM2 FEP would be less dense than the tightly curled area due to the expected lower temperature of exposure. The flat SM2 sample was less dense than the curled SM2 sample (2.155 vs. 2.183 g/cm^2, respectively). Heating the "flat" SM2 sample for 7 days resulted in an increase in the density to 2.177 g/cm^2. These results imply that the anomalous differences in density between the as-retrieved SM1 FEP and SM2 FEP were due to the differences in the temperature extremes experienced on-orbit.

These results also suggest that the HST samples have undergone chain scission while in space and that heating either on-orbit or in ground facilities to 200 °C enables the shorter chains to shift resulting in more dense packing (increased crystallinity) and a corresponding density increase.

Thermal cycling at the nominal temperature extremes experienced on HST (such as experienced by the SM1 FEP) did not cause a change in density as can be seen by the data in Table 3. Thermal cycling at the low temperatures experienced by anti-solar facing surfaces on HST (which are also embrittled) also did not cause a change in the density.

Table 3. Density of Thermal Cycled Al-FEP Samples.

Sample	Thermal Cycling Conditions	Density As-Received (g/cm^3)	Density after Thermal Cycling (g/cm^3)	Density Change
5 mil Al-FEP	-100 to +50 °C 6,000 cycles	2.141	2.141	0.000
5 mil Al-FEP (GSFC FEP)	-196 to +74 °C* 20,000 cycles	2.125	2.127	0.002
FEP7B, Mo x-ray Irradiated Area	-196 to +74 °C* 2,688 cycles	2.147	2.146	-0.001

* Cycled to +130 °C every 7^{th} cycle

Pristine Al-FEP samples were heated to 200 °C and their densities were found to increase with heating. But, the increase in density of the pristine heated samples was less than for the space exposed samples. For example, pristine FEP increased in density by 0.020 g/cm^2 after 21 days (0.94%), while the 16,670 ESH SM1 sample increased in density by 0.030 g/cm^2 after 21 days (1.41%) (Table 4). Samples of pristine FEP were exposed to 200 °C for 1-7 days. These data, shown in Figure 4, indicate that the majority of density increase occurred within 72 hours of heating. An additional sample heated for 21 days showed no additional density increase than experienced after 3 days of heating. Samples of pristine FEP and SM1 FEP (11,339 ESH) were also exposed to temperatures ranging from 50 °C to 200 °C for 21 days to see what temperature causes an increase in density. The results are plotted in Figure 5. There appears to be a very small increase in density with increasing temperature up to 125 °C, then at a temperature of 150 °C and above, the density increases significantly. This was true for both the pristine and the SM1 FEP. The rate at which the density increases was greater for the SM1 FEP than for the pristine FEP, in both regions of the graph. For example, the slope of the SM1 line from 125 °C to 200 °C is 3.34×10^{-4} g/cm^2 °C, while it is 2.22×10^{-4} g/cm^2 °C for pristine FEP. These results indicate that heating at temperatures of 150 °C and above, without prior radiation or space exposure, can result in an increased density of FEP. It has been reported that elevated temperature exposure can cause chain scission in polymers.[13] These results also indicate that prior space exposure causes greater density increases with heating than for unexposed FEP. This supports the idea that space exposure (at nominal temperatures of 50 ºC) causes chain scission in the polymer structure, and that with sufficient heating the shorter chains can move into more densely packed areas.

The densities of two x-ray exposed FEP samples (FEP4D and FEP7D), with tensile properties similar to SM1 FEP were determined. A tensile sample from the same exposure run as FEP7D had an elongation to failure relative to pristine FEP of 10.4% (SM1 MSS-D was 20.8% using the same equipment). The as-irradiated samples had densities similar to pristine Al-FEP, as seen in Table 2. Thermal cycling of a Mo x-ray irradiated sample (FEP7B) at anti-solar facing temperature extremes caused no change in the density of the sample (see Table 3) similar to the pristine thermal cycled samples. Heating the irradiated samples at 200 °C (13 days) resulted in an increase of the density by 0.032 g/cm^2, this is the same density increase experienced by heating SM1 MSS-D. An independent study conducted by Gaier et al., on higher energy x-ray exposure of FEP found density and heating results consistent with those found in this study.[9]

Radiation exposure of FEP has been reported by Rosenberg et al., to cause chain scission in Teflon® FEP.[14] The x-ray exposure results support the idea that irradiation induces chain scission in FEP on HST while in space. Also, both the SM1 FEP (MSS-D) and the x-ray exposed FEP (FEP7A) experienced decreases in the ultimate tensile strength compared to pristine FEP (decreases of 29.2% and 22.4%, respectively). Decreases in the tensile strength of polymers exposed to irradiation are generally attributed to a chain-scission mechanism.[13,15] A study conducted by Bowers et al., found that FEP cross-links when irradiated above the glass transition temperature (Tg = 80 °C).[16] Therefore, once the FEP curls, cross-linking many also play a role in the degradation mechanism, but by then the polymer has been extensively embrittled and has already displayed a loss of tensile strength from scissioning.

Table 4. Density of Pristine and SM1 FEP after 200°C Heating.

Sample	Temperature during Space Exposure	Density As-Received (g/cm^3)	Density after 200°C (g/cm^3)	Heating Density Change	Heating Time (Days)
Al-FEP	-	2.141	-	-	-
Al-FEP	-	2.138	2.149	0.011	1
Al-FEP	-	2.138	2.153	0.015	2
Al-FEP	-	2.138	2.158	0.020	3
Al-FEP	-	2.138	2.158	0.020	4
Al-FEP	-	2.138	2.158	0.020	5
Al-FEP	-	2.138	2.159	0.021	6
Al-FEP	-	2.138	2.160	0.022	7
Al-FEP	-	2.138	2.158	0.020	21
SM1 MSS-D (11,339 ESH)	-100 to +50 °C	2.140	2.171	0.031	7
SM1 MSS-D	-100 to +50 °C	2.141	2.173	0.032	9
SM1 MSS-D	-100 to +50 °C	2.140	2.169	0.029	14
SM1 MSS-D	-100 to +50 °C	2.135	2.165	0.030	21

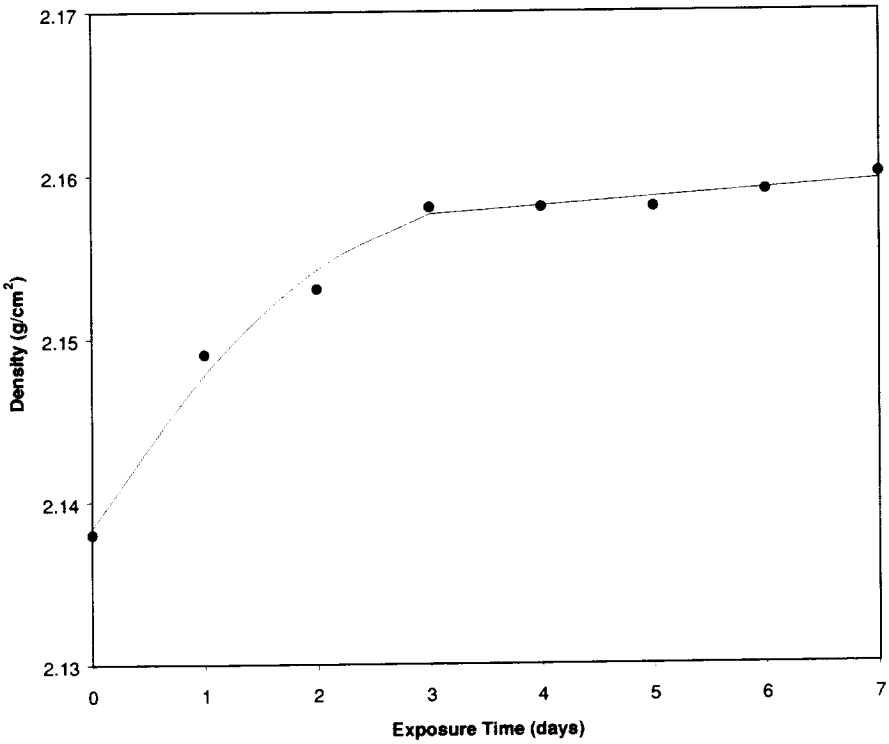

Figure 4. Effect of heating for 1 to 7 days at 200°C on the density of Al-FEP.

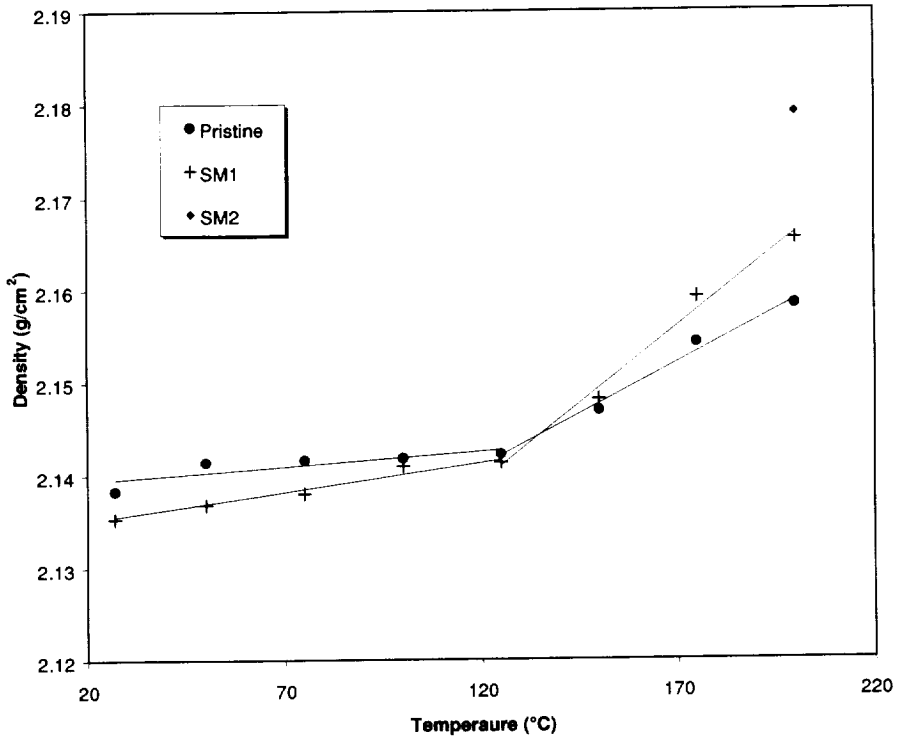

Figure 5. Effect of heating temperature (3 week exposure) on the density of pristine FEP and SM1 FEP.

The effects of long term exposure of FEP at 200 °C is of interest. The mechanical properties of FEP (both ultimate tensile strength and percent elongation to failure) have been found to decrease when tested at 200 °C.[17] The effect of long term heating at 200 °C on the tensile properties of FEP is currently under investigation. Preliminary data indicates that long term elevated temperature exposure can cause a decrease in mechanical properties of FEP when tested at room temperature, which further indicates that chain scission is the primary mechanism occurring at elevated temperature.

The percent crystallinity of Teflon® can be calculated based on its density.[18] Using this technique, the percent crystallinity of the as-received and heated, pristine and HST samples have been obtained, and are presented in Table 5. It can be seen from this data, that a small increase in the density corresponds to a significant increase in the percent crystallinity of the polymer. Pristine Al-FEP had a crystallinity of 49.6 to 50.6 %, and heating at 200 °C increased the crystallinity to 56.8 %. Heated SM1 FEP (MSS-A) had a 61.5 % crystallinity, and as-received SM2 FEP had a 64.6 % crystallinity. This is an increase in the percent crystallinity of 21.5 % and 27.3 % compared to pristine FEP, respectively.

Table 5. Density and Corresponding Percent Crystallinity.

Sample	As-Received Density (g/cm^3)	As-Received Percent Crystallinity	Heating (days)	Heated Density (g/cm^3)	Heated Percent Crystallinity
Al-FEP	2.138-2.141	49.6-50.6	1	2.149	53.2
Al-FEP	2.138-2.141	49.6-50.6	3	2.158	56.2
Al-FEP	2.138-2.141	49.6-50.6	7	2.160	56.8
Al-FEP	2.138-2.141	49.6-50.6	21	2.158	56.2
SM1 MSS-G (4,477 ESH)	2.141	50.6	9	2.163	57.8
SM1 MSS-F (6,324 or 9,193 ESH)	2.139	49.9	9	2.166	58.8
SM1 MSS-C (9,193 or 6,324 ESH)	2.141	50.6	5	2.166	58.8
SM1 MSS-D (11,339 ESH)	2.141	50.6	9	2.173	61.1
SM1 MSS-A (16,670 ESH)	2.143	51.2	9	2.174	61.5
SM2 Curled (33,638 ESH)	2.183	64.4	5	2.184	64.7
SM2 Flat (33,638 ESH)	2.155	55.2	7	2.177	62.4
FEP4D Al x-ray	2.143	51.2	13	2.175	61.8
FEP7D Mo x-ray	2.147	52.6	13	2.179	63.1

3.2 Solid State NMR Results

The ^{13}C spectra for all three samples (Pristine FEP, SM1 FEP and SM2 FEP) consist of three peaks at 98, 115, and 122 ppm (frequency shift in ppm from a tetramethylsilane standard) arising from CF, CF_2, and CF_3 groups, respectively, as shown in Figure 6. A comparison of the SM1 and SM2 FEP with the pristine material shows that there are no new peaks observable in the NMR spectrum after space exposure. These results show that if there is formation of new –CFX- species they are present at low levels (<5% of carbon sites). The three spectra also show little change in terms of the relative intensities of the three peaks. These results, in conjunction with the fact that there is little or no additional CFX species, indicate that there is no large-scale chemical modification of the material. The ^{13}C spectra for all three samples did not change after heating at 190°C (there were no indications of new peaks or changes in the relative intensities of the $-CF_x-$ peaks). Therefore, heating the samples at this temperature did not cause any significant chemical changes to the FEP films, consistent with the as-received SM2 results.

The T_{CF} curve, shown in Figure 7, is a plot of the ^{13}C signal intensity versus the cross polarization time. The rate at which the intensity increases is dependent on the $^{13}C - ^{19}F$ dipolar coupling, which in turn is dependent on the molecular motion present. The tighter the chain packing and the less kHz regime motion that is present, the more rapid is the rise in intensity. The T_{CF} curves for the pristine and SM1 samples are nearly identical, indicating that the two samples have a similar structural morphology. However, the T_{CF} curve for the SM2 sample is different from the SM1 sample, the intensity reaches a peak at ≈1 ms versus 2 ms. These results indicate that there is less molecular motion and tighter chain packing in the SM2 sample. These changes in morphology may a rise either from material changing from amorphous to crystalline or by the material becoming more ordered within the amorphous domains.

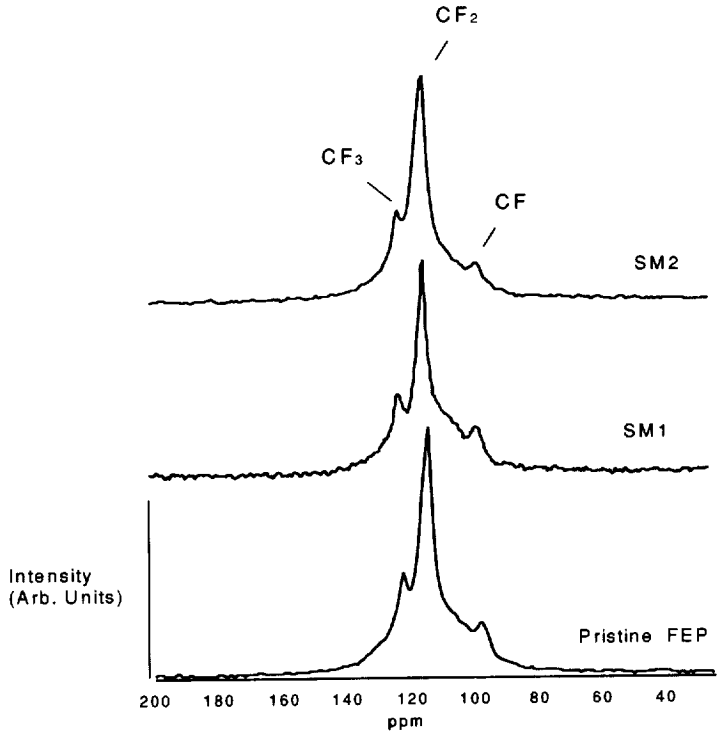

Figure 6. ^{13}C spectra of as-received pristine FEP, SM1 FEP and SM2 FEP.

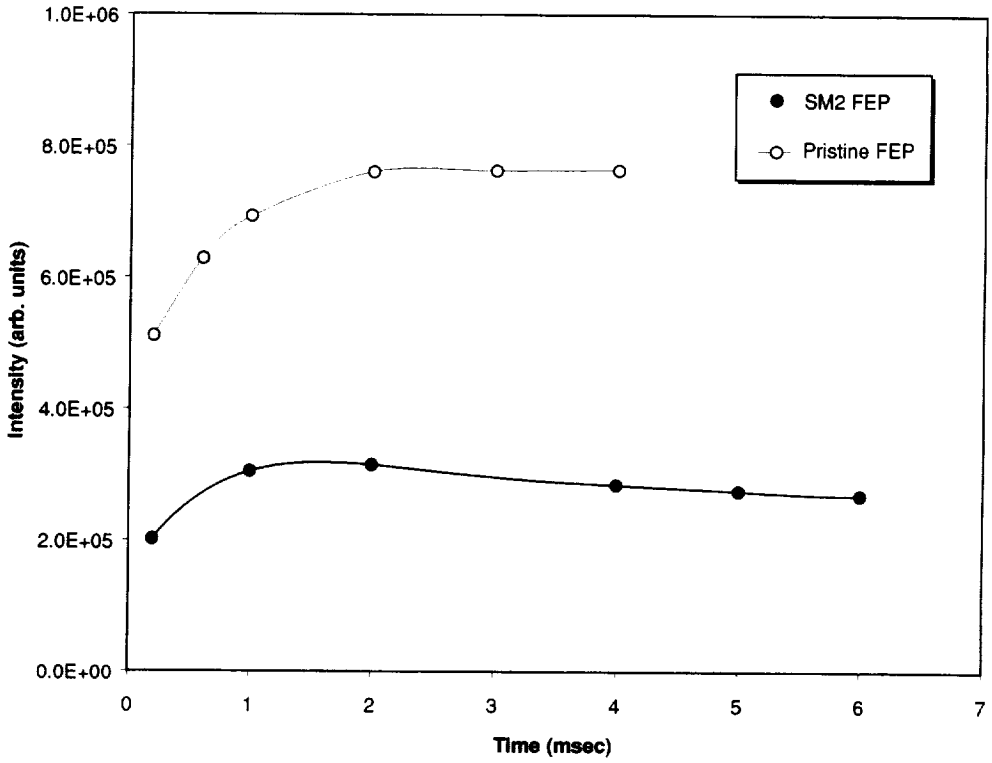

Figure 7. T_{CF} Curves for as-received pristine FEP and SM2 FEP.

The measurement of T1ρ(C) values provides insights into the morphology and morphological changes occurring in the polymer by probing polymer chain dynamics. As the polymer chains become more tightly packed, either by changing from amorphous to crystalline or by becoming more ordered in the amorphous domains, the extent of polymer motion is reduced. A reduction in motion is observed as an increase in the magnitude of T1ρ(C). The T1ρ(C) for the pristine and SM1 samples are nearly equal at ≈34 msec, showing that there is little change in the polymer morphology upon the initial exposure period. However, for the SM2 sample the T1ρ(C) has increased to 43 msec, showing an increase in the extent of crystalline and near-crystalline regions in the SM2 films. The T1ρ(C) values are listed in Table 6. Heating the pristine material at 200 °C in the lab for 6 days shows only a small increase in T1ρ(C) to 38 msec, whereas a similar heating of the SM1 sample causes an increase of T1ρ(C) to 41 msec, as seen in Table 6. In contrast, heating the SM2 sample to 200 °C results in little change in its T1ρ(C) values, showing that additional heating does not cause any significant change in the polymer morphology. These results implicate heating of the material to 200 °C as an important factor in causing the observed morphology changes. However, these changes in morphology are enhanced if the film endures exposure in space prior to the film heating, showing that there is some chemical modification occurring in the space exposed films allowing a larger change in morphology. While the exact chemical changes occurring can not be verified, the results from the NMR characterization are consistent with chain scission in the FEP films. More details of NMR characterization of these materials can be found in reference 12.

Table 6. T1ρ(C) values for FEP films.

Sample	T1ρ(C) before heating CP= 2 msec	T1ρ(C) After heating CP= 2 msec	% Change in T1ρ(C)
Pristine FEP	35	38	8.6
SM1	33	41	24.2
SM2	41	43	4.9

The results from the NMR characterization were consistent with the density results. Both characterization techniques showed the as-received SM1 FEP to be structurally similar to pristine FEP, and SM2 FEP to be more tightly packed or more crystalline. Both techniques showed that heating to 200 °C produces a change in the morphology of both the pristine and SM1 FEP, with the SM1 FEP experiencing a greater change than the pristine FEP. When the percent change in the T1ρ(C) data upon heating (listed in Table 6) was compared to the percent change in the crystallinity upon heating (listed in Table 7) it is interesting to see the consistency in the values for the samples. The pristine FEP experienced approximately a 10% change in both characterization techniques upon exposure to 200 °C. The change in the SM1 material (which has undergone prior space exposure) with heating to 200 °C experienced approximately twice the change of the pristine material, and the SM2 FEP changed very little in both techniques.

Table 7. Percent Change in Percent Crystallinity of Heated Pristine and HST FEP.

Sample	Heating Time (Days)	% Crystallinity	% Crystallinity after 200°C	% Change in % Crystallinity
Pristine FEP	7	50.6	56.8	12.3
SM1 MSS-D	9	50.6	61.1	20.8
SM2 Curled	5	64.4	64.7	0.5

4. CONCLUSIONS

The results of density and NMR studies of pristine FEP and FEP retrieved after long term space exposure on the HST have provided insight to the damage mechanism of Teflon® FEP in space. The results indicated that irradiation of Teflon® FEP in space causes chain scission, resulting in FEP embrittlement. Heating at nominal temperatures experienced on HST resulted in no change in the density or crystallinity of FEP. But that sufficient heating, such as experienced by the retrieved curled SM2 sample, allows increased mobility of the space-environment-induced scissioned short chains, with resulting increased crystallinity and density. The percent crystallinity of retrieved SM2 FEP was found to be 27% higher than the percent crystallinity of pristine FEP. Heating of pristine FEP at 200 °C was also found to result in increases in crystallinity and density, but the increases were not as great as for the heated space exposed samples which experience chain scissioning due to irradiation in space.

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13. ABSTRACT ***(Maximum 200 words)***

Metallized Teflon® FEP (fluorinated ethylene propylene) thermal control material on the Hubble Space Telescope (HST) is degrading in the space environment. Teflon® FEP thermal control blankets (space-facing FEP) retrieved during the first servicing mission (SM1) were found to be embrittled on solar facing surfaces and contained microscopic cracks. During the second servicing mission (SM2) astronauts noticed that the FEP outer layer of the multi-layer insulation (MLI) covering the telescope was cracked in many locations around the telescope. Large cracks were observed on the light shield, forward shell and equipment bays. A tightly curled piece of cracked FEP from the light shield was retrieved during SM2 and was severely embrittled, as witnessed by ground testing. A Failure Review Board (FRB) was organized to determine the mechanism causing the MLI degradation. Density, x-ray crystallinity and solid state nuclear magnetic resonance (NMR) analyses of FEP retrieved during SM1 were inconsistent with results of FEP retrieved during SM2. Because the retrieved SM2 material curled while in space, it experienced a higher temperature extreme during thermal cycling, estimated at 200 °C, than the SM1 material, estimated at 50 °C. An investigation on the effects of heating pristine and FEP exposed on HST was therefore conducted. Samples of pristine, SM1, and SM2 FEP were heated to 200 °C and evaluated for changes in density and morphology. Elevated temperature exposure was found to have a major impact on the density of the retrieved materials. Characterization of polymer morphology of as-received and heated FEP samples by NMR provided results that were consistent with the density results. These findings have provided insight to the damage mechanisms of FEP in the space environment.

14. SUBJECT TERMS

Thermal exposure; Environmental exposure; Multilayer insulation; Degradation; Embrittlement; Teflon® FEP; Hubble Space Telescope, Low Earth Orbit durability

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